

(51) International Patent Classification ⁶ : B01D 19/00, C02F 1/02, 1/72, 11/08	A1	(11) International Publication Number: WO 97/36663
		(43) International Publication Date: 9 October 1997 (09.10.97)

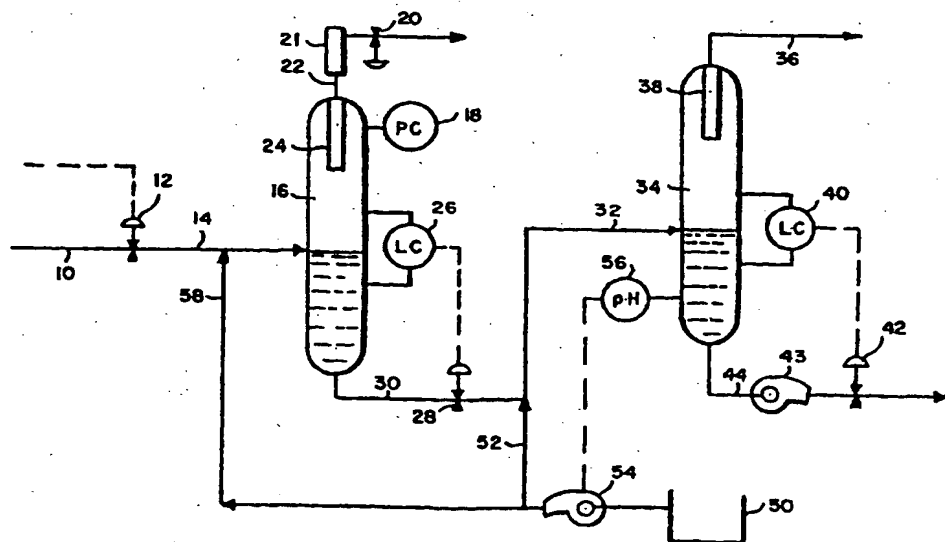
(74) Agent: LANDO, Peter, C.; Wolf, Greenfield & Sacks, P.C.,
600 Atlantic Avenue, Boston, MA 02210 (US).

(43) International Publication Date: 9 October 1997 (09.10.97)

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: TWO-STAGE SEPARATION PROCESS



A process is disclosed for producing an oxidized liquid phase with minimal dissolved gases from a wet oxidation treatment system. The oxidation mixture exiting from the treatment system enters a first separator vessel operated at superatmospheric pressure where gaseous and liquid phases separate. The superatmospheric gases are routed to further treatment or discharged to the environment. The aqueous phase flows to a second separator vessel operated at essentially atmospheric pressure where additional dissolved gases separate from the liquid phase. The gases are discharged and the liquid phase is suitable for storage or further treatment. Provision for adjusting the pH of the liquid phase during the separation process is also disclosed.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

TWO-STAGE SEPARATION PROCESS

1. Field of the Invention

This invention is concerned with a multiple stage separation process for gaseous and
5 liquid phases from a wet oxidation system.

2. Description of the Related Art

Wet oxidation is a well known process for treatment of aqueous wastewaters. The process involves heating a mixture of the wastewater plus an oxygen-containing gas to elevated temperature and pressure to effect oxidation of oxidizable substances contained in the
10 wastewater. All wet oxidation systems include one or more pressure control valves to regulate the flow of liquid, solids and gases from the high pressure part of the system to the low pressure part of the system.

Ledding, in U.S. Patent No. 3,150,105, discloses a blow down tank or other suitable decompression vessel which receives the cooled regenerated carbon slurry from a wet oxidation
15 reactor. No further description of the blow down tank is provided.

In U.S. Patent No. 3,994, 702, Schweimanns et al. disclose a flooded sluicing chamber for ash removal from a pressurized gasification chamber.

Meidl et al., in U.S. Patent No. 4,620,563 disclose a blowdown pot with an inlet pressure control valve through which the pot receives unwanted residue e.g., ash from a high pressure
20 chemical reactor. This reactor residue can be continuously or semi-continuously blown out from the high pressure, high temperature chemical reactor into the relatively low pressure blowdown pot which includes means for maintaining a liquid level therein, thus minimizing steam flashing vessel wear.

In U.S. Patent No. 5,011,114, Depuydt et al. disclose a pressure control valve with a
25 valve seat and support assembly which extends beyond the valve body to prevent erosion by the blowdown slurry. The apparatus also includes a displacement-compensating seal between the valve and receiving vessel to allow for thermal expansion and contraction during the blowdown cycle while maintaining the integrity of the seal.

Lehmann et al. in U.S. Patent No. 5,389,264 disclose a process for dissipating the energy
30 of a wet oxidation mixture after that stream traverses a pressure control valve. The depressurized stream is discharged into a phase separator vessel containing a gas phase and a liquid phase. The pressure control valve is positioned to discharge the oxidation mixture at a selected orientation

below the surface level of the liquid phase in the vessel. This dissipates the energy of the mixture and prevents erosion of the phase separator vessel.

In general, a single stage separator vessel operating essentially at atmospheric pressure is employed in a wet oxidation flow scheme to effect separation of liquid and gaseous phases once the oxidized effluent mixture traverses the pressure control valve which maintains system operating pressure. This single stage separation produces a liquid effluent which may not be suitable for all applications. For example, significant amounts of gases, such as CO₂, N₂, and O₂, can remain dissolved in the separated liquid phase. When this liquid effluent is stored in a covered collection tank, these dissolved gases can come out of solution and collect within that tank, causing operational problems.

Likewise, the separated gas phase, essentially at atmospheric pressure, may require further treatment which entails movement of the whole volume of gas through that treatment process. Transfer of the gas requires expenditure of energy in some form, such as a blower, a compressor, or the like, entailing additional operating expense. Further, the gas phase from a single stage separator at atmospheric pressure contains a significant amount of water vapor. The water vapor adds expense to downstream gas phase treatment such as passage through a high temperature afterburner. Condensation of this water vapor can result in corrosion to the equipment in contact with the gas phase as well.

Applicants have devised a process which produces a liquid effluent which does not have the drawbacks of the gas saturated effluent discussed above. Likewise, the resulting separated gas phase is obtained at a moderate pressure which allows the gas to be routed to further treatment without input of additional energy, and with a reduced water vapor content which simplifies further treatment.

SUMMARY OF THE INVENTION

The gas/liquid mixture from a wet oxidation process operating at elevated temperature and pressure is cooled by flowing through a process heat exchanger or other cooling means. The cooled oxidation mixture then traverses a pressure control valve to reduce the pressure to that sufficient to move the gas phase to any downstream treatment. The partially depressurized mixture flows into a first phase separation vessel where noncondensable gases are separated from liquid which is still saturated with gases at this operating pressure. The first separator has an upper gas outlet conduit controlled by a pressure controller and a pressure control valve and a

lower liquid outlet conduit controlled by a level controller and a level control valve. The liquid phases, saturated with gases, is depressurized through the liquid level control valve and flows to a second phase separation vessel operated essentially at atmospheric pressure. The depressurization removes the dissolved gases from the liquid phase in the second separator vessel. The gas phase from the second separator may be routed to further treatment or discharged to the environment. The liquid phase, now containing little if any dissolved gases may be stored in a suitable vessel or discharged to further treatment if necessary. This staged separator sequence fully degasses the liquid and prevents gases from collecting in an effluent storage vessel where the presence of a gas phase is undesirable. The pressurized gases from the first separator vessel still contain some energy, and need only to be routed to further treatment in this relatively low pressure state. In a further embodiment of the invention, a pH adjusting substance is added to the liquid effluent to provide a liquid phase pH suitable for further treatment or discharge of the liquid effluent.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 shows a schematic diagram for the two stage separation process applicable to the effluent from a wet oxidation system.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Wet oxidation systems operate at 150° - 350°C and at pressures of at least 100 psig, up to about 3,500 psig. Referring to FIGURE 1, an oxidized cooled wet oxidation mixture in a conduit 10 flows through a pressure control valve 12 which depressurizes the oxidation mixture to a pressure sufficient to move the gas phase to any downstream treatment, including passage through all necessary control valves. Typically a pressure of about 10 psig is sufficient for this purpose, although higher pressures may be suitable or even required in some situations. The partially depressurized mixture flows through another conduit 14 and into a first separator vessel 16 where the gaseous phase and the liquid phase separate. The pressure within the first separator vessel is maintained at the desired superatmospheric pressure (at least about 10 psig) by a pressure controller 18 which operates a pressure control valve 20. This valve 20 controls the gaseous phase flow through the outlet conduit 22 exiting near the top of the separator vessel 16. A demister device 24 may assist in phase separation within the vessel. Optionally, a gas/liquid scrubber 21 may be located between the first separator vessel 16 and the pressure control valve

20 to condition the gas stream flowing through the outlet conduit 22 prior to the gas phase traversing the pressure control valve 20.

The liquid phase is maintained at the desired level in the vessel 16 by a level controller 26 which operates a level control valve 28. This valve 28 controls the liquid phase flow through the outlet conduit 30 exiting near the bottom of the first separator vessel 16.

The majority of the noncondensable material in the oxidized effluent mixture enters the gaseous phase in the first separator vessel 16. The liquid phase, however, is saturated with gases at the operating pressure of this first stage of separation which ranges upward from about 10 psig. The great majority of the gases are separated into the gaseous phase. As additional liquid and gases enter the separator vessel 16, the pressure increases and the liquid level rises. The pressure controller 18 maintains the desired pressure (at least about 10 psig) by modulating the flow of the gaseous phase through the conduit 22 using the pressure control valve 20. As the liquid level rises, which is sensed by the level controller 26, a portion of the liquid flows through the exit conduit 30, through the level control valve 28, and through a conduit 32 to a second separator vessel 34 operated essentially at atmospheric pressure. Thus, the operating pressure and liquid level within the first separator vessel are maintained within selected operating parameters.

Within the second separator vessel 34, the gas saturated liquid phase encounters essentially atmospheric pressure conditions and the soluble gases are transferred to the gaseous phase which exits the vessel 34 via a vent conduit 36. A demister 38 may be used to retain fine droplets of liquid in the vessel 34. The liquid phase in the second separator is maintained at the desired level in that vessel 34 by a second level controller 40 which operates a second level control valve 42. This valve 42 controls the liquid phase outlet flow through the conduit 44 exiting near the bottom of the second separator vessel 34. Optionally, a centrifugal pump 43 connected in the liquid phase outlet conduit 44, ahead of the level control valve 42, may assist in removing the liquid from the second separator vessel 34.

As mentioned earlier, the majority of the gaseous components from the wet oxidation mixture are separated into a first gas phase in the first separator vessel 16. This pressurized gas can be routed to further treatment without imparting additional energy to the gas. Further, there is economy in pressurized gas handling in that smaller sized vessels and piping can be used, providing an economic benefit for the process. Additionally, the pressurized gases from the first separator vessel have a reduced water vapor content compared to the gases discharged from a

system without a pressurized separator. The reduced water vapor content decreases the cost of downstream gas phase treatment, such as passage through a high temperature afterburner.

Likewise, corrosion of the gas phase handling equipment in contact with water condensed from the gases is minimized by low humidity gases. This pressurized separation thus improves the handling and further treatment of these pressurized gases.

The volume of gas phase generated in the second separator vessel 34 is generally quite small. Only the gases soluble in the liquid phase entering from the first separator vessel are liberated within the second separator vessel. The liquid phase exiting from the second separator vessel 34 via the exit conduit 44 is essentially free of excess dissolved gases. There is no supersaturation of the separated liquid phase with gases as can occur with a single stage separator system. Thus any problems associated with dissolved gases coming out of solution from the oxidized liquid phase in downstream treatment or storage are avoided.

In a further embodiment of the invention, there may be situations where it is necessary to adjust the pH of the oxidized liquid phase to a preselected range prior to discharge from this phase separation process. To accomplish this pH adjustment, a pH adjusting substance, either acidic or basic, is added to the liquid phase after it has passed from the first separator vessel 16 through the level control valve 28. The pH adjusting substance, stored in a tank 50, is added to the liquid in the conduit 32 from a conduit 52 supplied from a pump 54 drawing from the tank 50. The amount of pH adjusting substance added is controlled by a pH controller 56 which monitors pH downstream of the addition point, such as within the second separator vessel 34.

For example, the oxidized liquid phase from the first separator vessel 16 may have a basic pH and further biological treatment requires a pH near neutral. Thus the pH controller 56 adjusts the addition of acidic material to maintain the liquid pH within the second separator vessel in the pH range of 6 to 8. In this case, an acid solution, such as sulfuric or hydrochloric acid, is added to the liquid in the conduit 32 to neutralize the basic components in the liquid and to produce a liquid with pH in the desired range, suitable for discharge. This particular pH adjustment may result in the generation of additional gases, such as CO₂, in the second separator vessel.

Similarly, an acidic liquid effluent may require the addition of a solution of basic substance, such as caustic soda or metal carbonate, to neutralize the liquid to a pH suitable for discharge.

Likewise, this pH adjustment may result in the generation of additional gases in the second separator vessel.

In an alternative embodiment of the invention, the pH adjusting substance may be added

to the oxidation mixture after it traverses the first pressure control valve 12, as it flows through the inlet conduit 14 to the first separator vessel 16. The pH adjusting substance is added from a conduit 58, also supplied from the pump 54 drawing from the tank 50 to produce an oxidized liquid in the first separator vessel with pH in the preselected range. In this embodiment, any
5 gases produced by the pH adjustment enter the gas phase found in the first separator vessel 16. In some cases it may be required to produce an oxidized liquid phase which is extremely acidic or basic. The pH adjusting steps described will accommodate such a requirement with little difficulty.

While the invention has been particularly shown and described with reference to a
10 preferred embodiment thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit and scope of the invention.

What is claimed is:

CLAIMS

1. A process for producing a wet oxidation liquid effluent with a minimal amount of dissolved gases therein, and a significant portion of a gaseous phase at superatmospheric pressure comprising:

- a) discharging a cooled wet oxidation mixture of liquid and gases from a wet oxidation system operating at elevated temperature and superatmospheric pressure, through a first pressure control valve to a first separator vessel maintained at a superatmospheric pressure lower than said oxidation system, to form a first noncondensed gas phase and a first oxidized liquid phase therein;
- b) discharging said first separated noncondensed gas phase from said first separator vessel to further treatment or to the environment;
- c) discharging said first separated oxidized liquid phase from said first separator vessel, through a first level control valve, to a second separator vessel maintained at essentially atmospheric pressure, to form a second noncondensed gas phase and a second essentially degassed oxidized liquid phase therein;
- d) discharging said second gas phase from said second separator vessel; and
- e) discharging said essentially degassed oxidized liquid phase from said second separator vessel.

2. The process according to claim 1 further comprising adjusting the pH of said first separated oxidized liquid phase to a preselected range by adding a pH adjusting substance to said oxidation mixture after said mixture passes through said first pressure control valve.

3. The process according to claim 2 wherein said pH adjusting substance is an acidic material.

4. The process according to claim 3 wherein said pH adjusting of said first liquid phase generates additional gases which enter said first noncondensed gas phase.

5. The process according to claim 2 wherein said pH adjusting substance is a basic material.

6. The process according to claim 5 wherein said pH adjusting of said first liquid phase generates additional gases which enter said first noncondensed gas phase.

7. The process according to claim 1 further comprising adjusting the pH of said first separated oxidized liquid phase from said first separator vessel to a preselected range by adding a pH adjusting substance thereto after said first separated oxidized liquid phase has discharged through said first level control valve.

8. The process according to claim 7 wherein said pH adjusting substance is an acidic material.

9. The process according to claim 8 wherein said pH adjusting of said first liquid phase generates additional gases which enter said second noncondensed gas phase.

10. The process according to claim 7 wherein said pH adjusting substance is a basic material.

11. The process according to claim 10 wherein said pH adjusting of said first liquid phase generates additional gases which enter said second noncondensed gas phase.

12. The process according to claim 1 wherein said superatmospheric pressure in said first separator vessel is maintained by a pressure controller and a second pressure control valve which modulates the discharge of said first gaseous phase therefrom.

13. The process according to claim 1 wherein said superatmospheric pressure in said first separator vessel is at least about 10 psig.

14. The process for producing a wet oxidation liquid effluent with a minimal amount of dissolved gases therein, and a significant portion of a gaseous phase at superatmospheric pressure comprising:

a) discharging a cooled wet oxidation mixture of liquid and gases from a wet oxidation system operating at elevated temperature and superatmospheric pressure, through a

first pressure control valve to a first separator vessel maintained at a superatmospheric pressure lower than said oxidation system, to form a first noncondensed gas phase and a first oxidized liquid phase therein;

5 b) discharging said first separated noncondensed gas phase from said first separator vessel to further treatment or to the environment;

 c) discharging said first separated oxidized liquid phase from said first separator vessel, through a first level control valve, to a second separator vessel maintained at essentially atmospheric pressure, to form a second noncondensed gas phase and a second essentially degassed oxidized liquid phase therein;

10 d) adding a pH adjusting substance to said first separated oxidized liquid phase after said first liquid phase has discharged through said first level control valve to produce a liquid with pH in a preselected range;

 e) discharging said second gas phase from said second separator vessel; and

15 f) discharging said essentially degassed oxidized liquid phase, with pH in a preselected range, from said second separator vessel.

15. The process according to claim 14 further comprising controlling the addition of said pH adjusting substance to said first separated oxidized liquid phase of step d) by means of a pH controller which monitors pH within said second separator vessel.

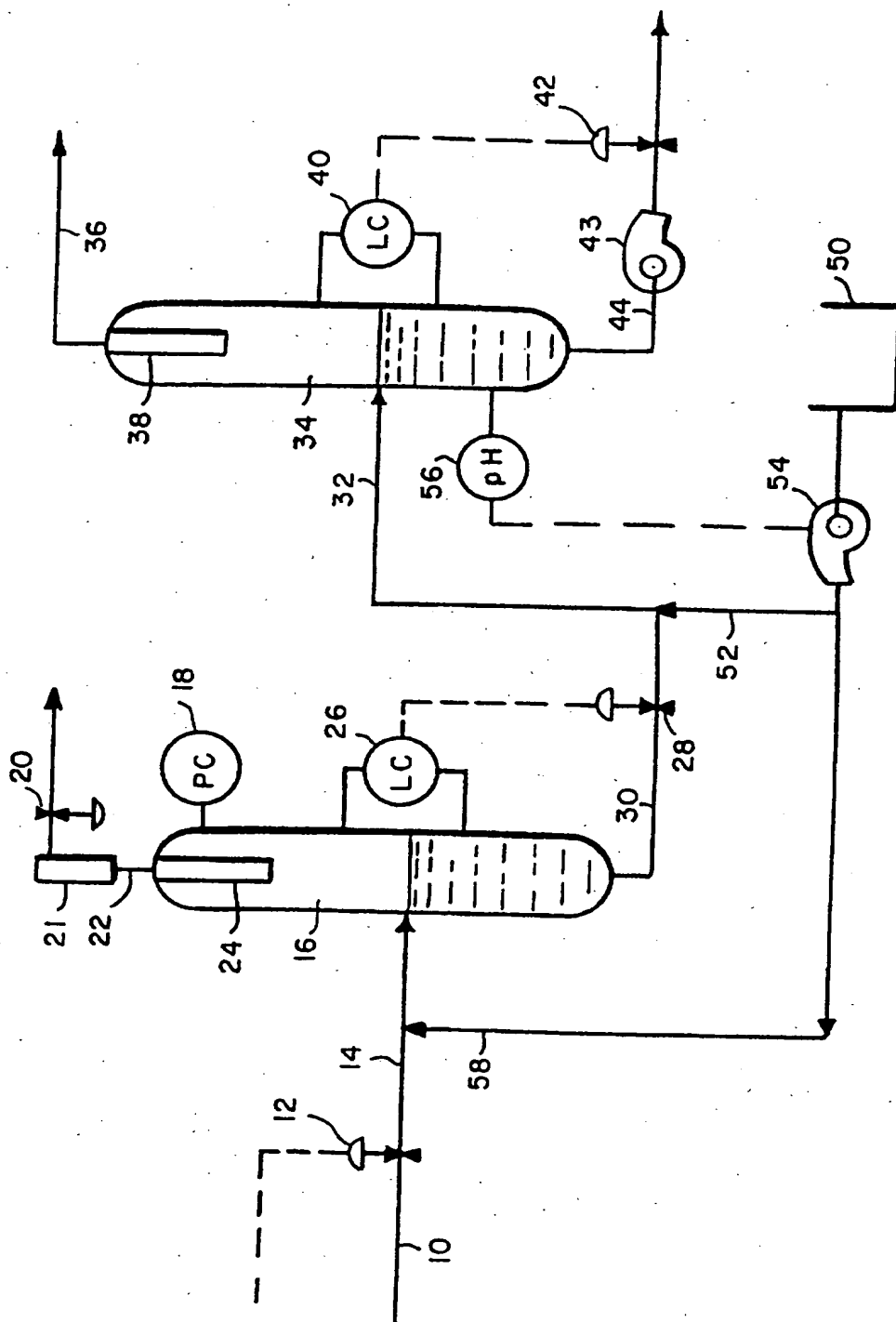


FIG. 1

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/05233

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01D19/00 C02F1/02 C02F1/72 C02F11/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B01D C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 94 11310 A (MODAR) 26 May 1994 see page 36; figure 4 ---	1,12
P,Y	US 5 544 672 A (PAYNE ET AL.) 13 August 1996 see the whole document ---	1,12
Y	US 5 389 264 A (LEHMANN ET AL.) 14 February 1995 cited in the application see the whole document ---	1
A	PATENT ABSTRACTS OF JAPAN vol. 004, no. 050 (C-007), 16 April 1980 & JP 55 022367 A (ASAHI CHEM IND CO LTD), 18 February 1980, see abstract --- -/--	1-15

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *&* document member of the same patent family

Date of the actual completion of the international search

22 July 1997

Date of mailing of the international search report

31. 07. 97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

De La Morinerie, B

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/05233

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 686 427 A (NIPPON SHOKUBAI) 13 December 1995 see page 12; figure 1; example 18 ---	1-15
A	US 3 630 002 A (BURRUS) 28 December 1971 see the whole document ---	12
A	EP 0 538 848 A (UREA CASALE) 28 April 1993 see the whole document -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/05233

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9411310 A	26-05-94	US 5232604 A	03-08-93
		AU 4797993 A	08-06-94
		CA 2148080 A	26-05-94
		EP 0666833 A	16-08-95
		JP 8503411 T	16-04-96

US 5544672 A	13-08-96	NONE	

US 5389264 A	14-02-95	NONE	

EP 686427 A	13-12-95	JP 8103655 A	23-04-96
		CN 1121322 A	24-04-96
		WO 9517958 A	06-07-95
		JP 7232063 A	05-09-95

US 3630002 A	28-12-71	CA 925768 A	08-05-73

EP 538848 A	28-04-93	CA 2081294 A	24-04-93
		CN 1073152 A	16-06-93
		RU 2056408 C	20-03-96
		US 5399755 A	21-03-95
